SWNT growth by the CoMoCAT method: Kinetic modeling, characterization of catalysts and nanotube product

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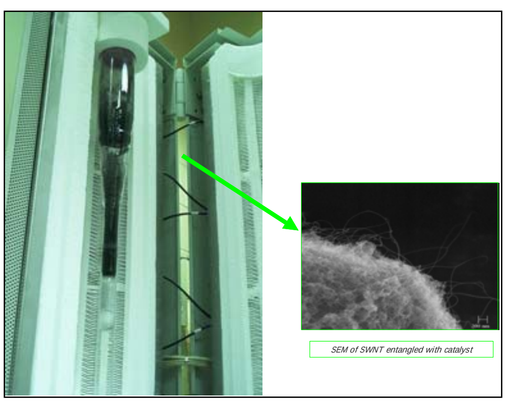
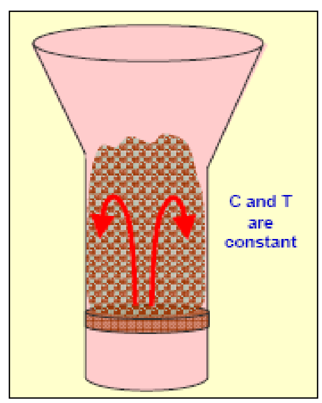
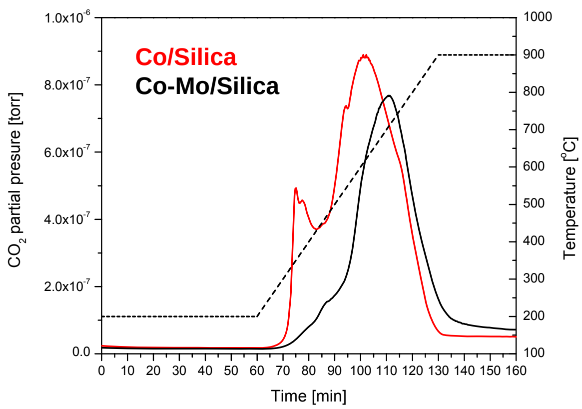
The CoMoCAT process





- CO disproportionation ($2\ CO \rightarrow C + CO_2$)
- Fluidized bed for uniformity
- Moderate temperatures = 700 – 900 C
- Moderate pressures = 1 – 10 atm

Mo retards the reactivity of Co towards CO



Temperature programmed reaction of oxidized Co and Co-Mo catalysts with CO (Evolution of CO_2)

Co/Silica:

$3\ CO + CoO \rightarrow CoC + 2\ CO_2$

$CoC \rightarrow Co + C$

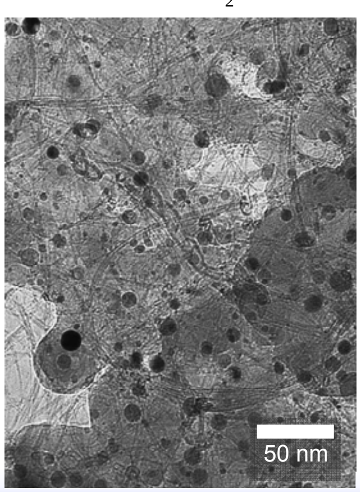
Co-Mo/Silica:

$\alpha\ CO + CoMoO_4 \rightarrow Co_xMo_yC + \beta\ CO_2$

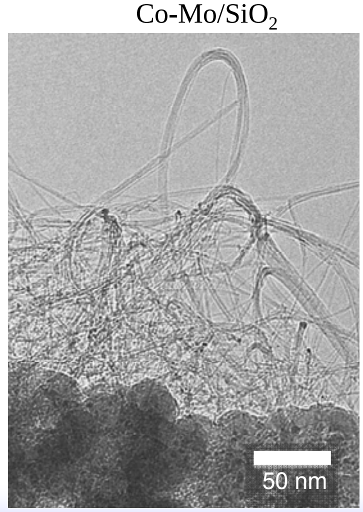
$Co_xMo_yC \rightarrow Mo_2C + Co$

Mo inhibits the sintering of Co

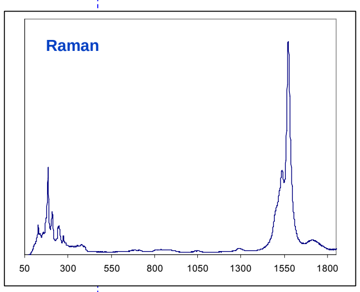
Co/SiO_2

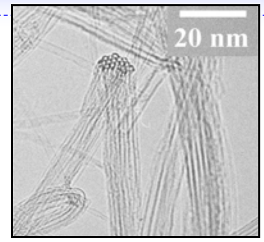


$Co\text{-}Mo/SiO_2$



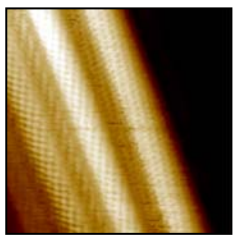
The CoMoCAT product

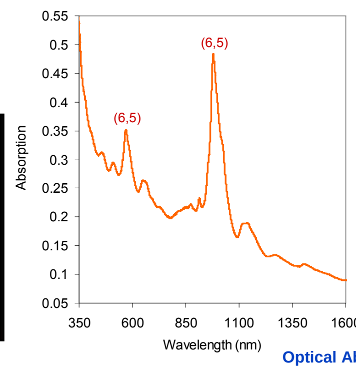




TEM

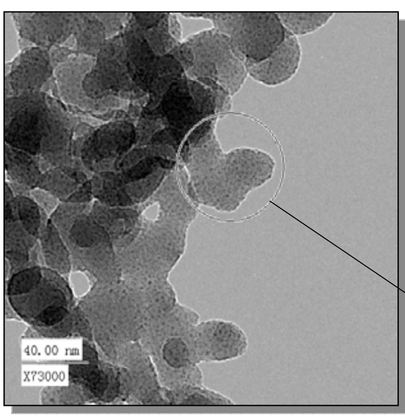
STM





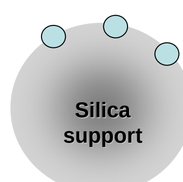
Optical Absorption

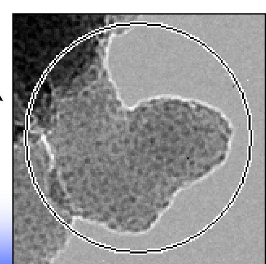
The CoMo catalyst



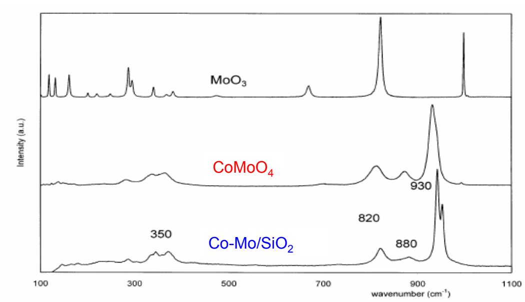
TEM CoMo catalyst (before reaction)

Dispersed Co Molybdate





Calcined CoMo catalyst - Before Reaction

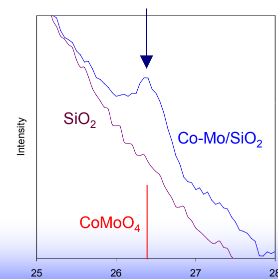


Raman Spectroscopy

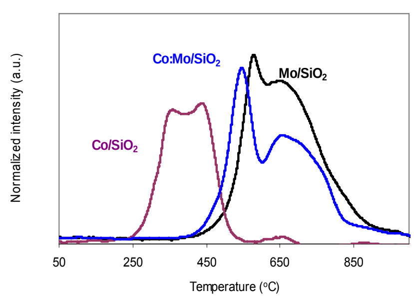
Bands at 930, 880 , 820, and 350 cm^{-1} typical of $CoMoO_4$.

X-ray Diffraction (XRD)

Small peak at 26° reveals the presence of highly dispersed $CoMoO_4$



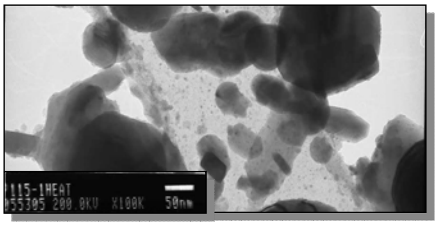
Calcined CoMo catalyst - Before Reaction



Temperature-Programmed Reduction (TPR)

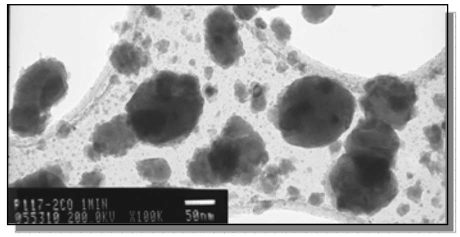
Absence of reducible Co at low temperature indicates that all the Co is in close interaction with Mo.

Catalyst Transformation During Reaction

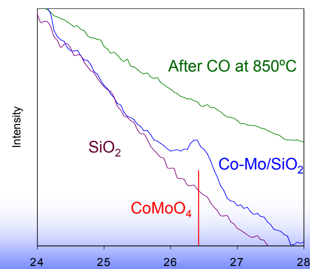


Before CO

TEM:
Attack of large $CoMoO_4$ crystals by CO at 850°C

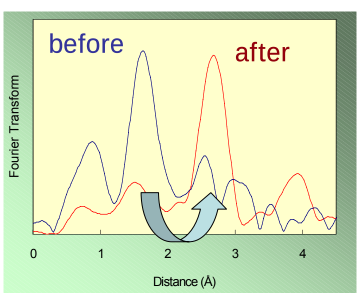


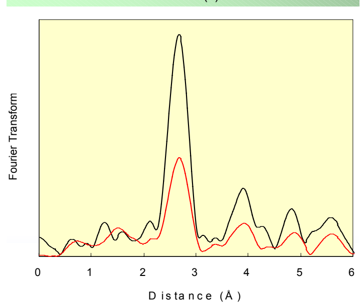
After 1 min in CO



X-ray Diffraction (XRD)
The 26º peak of $CoMoO_4$ disappears upon exposure to CO at 850°C

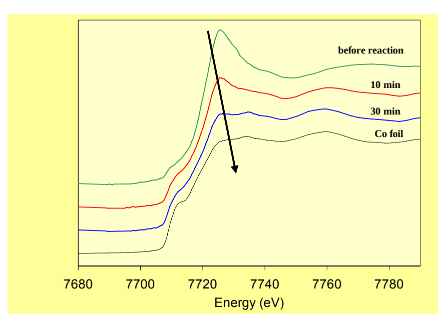
Catalyst Transformation During Reaction



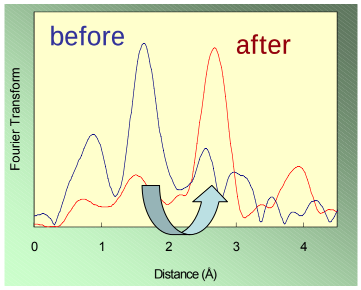


EXAFS:
K-edge of Mo (E_o = 20,000 eV). Mo-O bonds are converted to Mo-Mo with the length of those in Mo_2C

K-edge of Co (E_o = 7709eV)
Co^{2+} is converted to metallic Co(0)



Catalyst Transformation During Reaction



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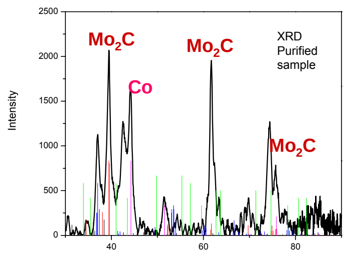
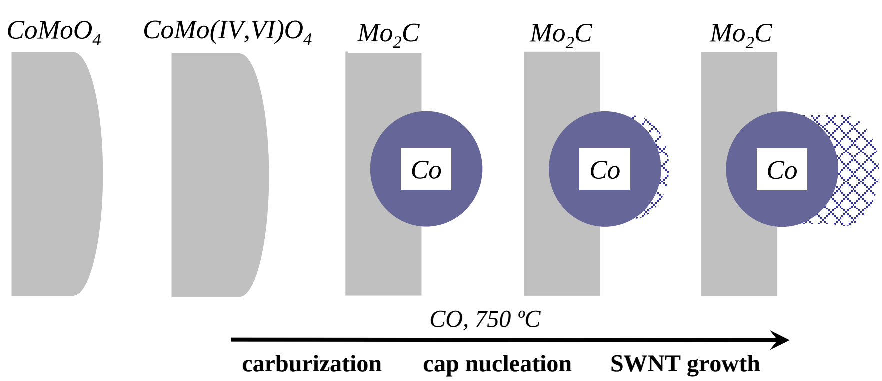
Co^{2+} is converted to metallic Co(0)



XRD of purified samples shows the presence of Mo_2C and Co metal in residual catalyst

Steps in the kinetic model of SWNT synthesis



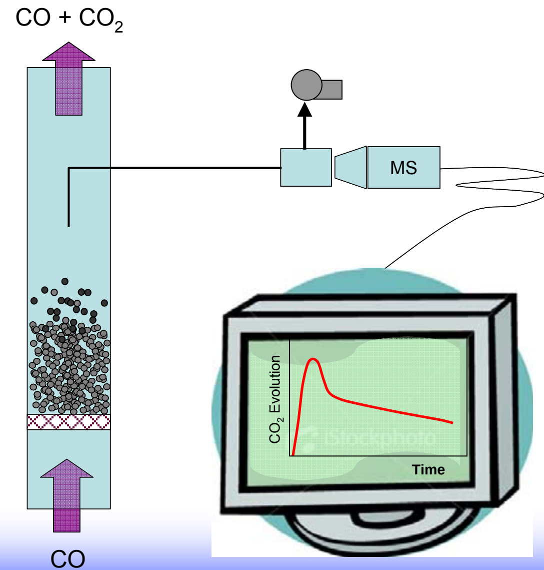
- Step 1: Carburization of the pre-reduced oxidic phase
- Step 2: Generation of active sites
- Step 3: CO dissociation over the surface of the reduced Co cluster
- Step 4: Nucleation and growth of SWNT
- Step 5: Growth Termination
  - Catalyst Deactivation
  - Hindrance Effect

Experimental measurement of SWNT growth rate

In the CO disproportionation reaction, the evolution of CO2 equals the depsotion of carbon:

2 CO → CO_2 + C

The rate of CO_2 evolution equals the SWNT growth rate



Carburization of the Co-Mo oxides

The rate of autocatalytic carburization is given by:

α CO + $CoMoO_4$ → Co_xMo_yC + β CO_2

Co_xMo_yC → Mo_2C + Co

$$r_{carb} = {d\alpha}/{dt} = M_{CT} * k_c (1-\alpha)(1+K\alpha)$$

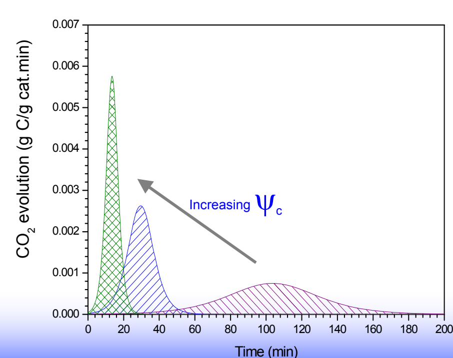
or

$$r_{C_{carb}} = M_{CT} \cdot \frac{(1+K)\cdot\psi_c \cdot \exp(-\psi_c \cdot t)}{(1+K\exp(-\psi_c \cdot t))^2}$$

where

$$\boxed{\psi_C = k_C\ (1+K)}$$

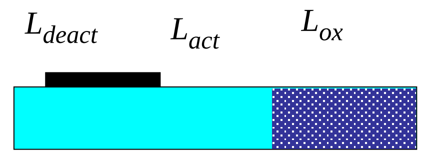
This initial CO_2 evolution does not correspond to SWNT growth .



Balance of active sites during reaction

Active site balance:

$$L_{ox} \xrightarrow{k_a} L_{act} \xleftrightarrow{k_d\,,\,k_r} L_{deact}$$



$$\frac{dL_{act}}{dt} = \psi_a \cdot L_{ox} - \psi_d \cdot L_{act} + \psi_r \cdot L_{deact}$$

definition $\boxed{a = \dfrac{L_{act}}{L_T}}$

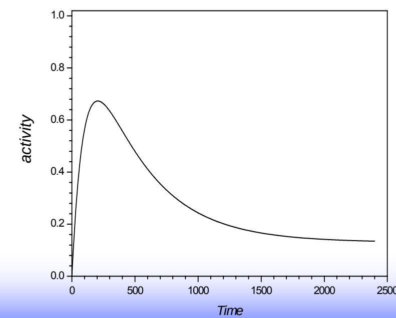
Catalyst activity (a) is then

$$a = a_S + \alpha_1 \cdot \exp(-\psi_a \cdot t) + \alpha_2 \cdot \exp(-\psi_G \cdot t)$$

$$\psi_G = \psi_d + \psi_r \quad ; \quad a_S = \frac{\psi_r}{\psi_d + \psi_r} = \frac{\psi_r}{\psi_G}$$

$$\alpha_1 = (1 - a_0) \cdot \left(\frac{\psi_a - \psi_r}{\psi_G - \psi_a} \right)$$

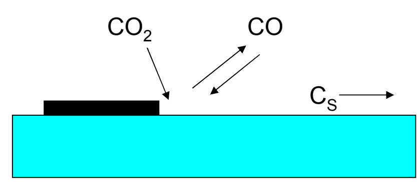
$$\alpha_2 = (a_0 - a_S - \alpha_1)$$



CO dissociation and C deposition

Boudouard reaction at interface 1:

$$(-r_{CO})_t = (-r_{CO})^0 \cdot a = k_1 \cdot \left(p_{CO} - \frac{p_{CO_2}}{K_{eq}\, p_{CO}} \right) \cdot a$$



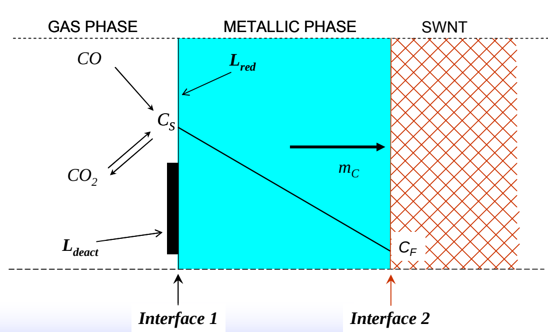
where k_1 and K_{eq} are given by:

$$k_1 = k_{1_0} \cdot \exp(-E_1/RT)$$

$$K_{eq} = \frac{k_1}{k_2} = \exp(-\Delta G/RT)$$

Diffusion from Interface 1 to Interface 2:

$$r_{C_{SWNT}} = \frac{dm_C}{dt} = k_C (C_S - C_F)$$

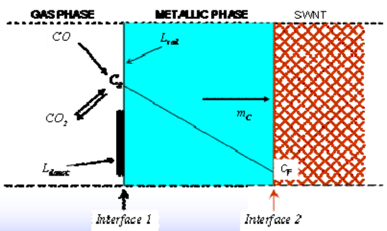


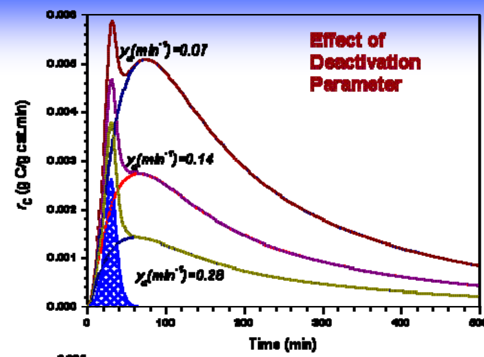
Growth Termination

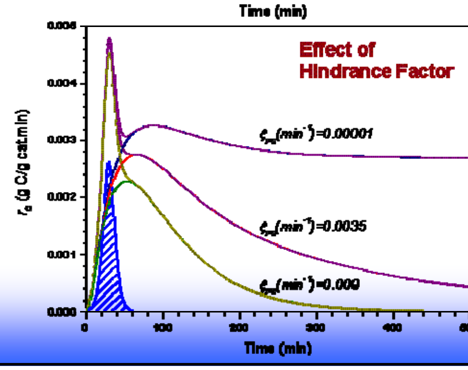
Two possible causes for growth termination:

a) Catalyst deactivation

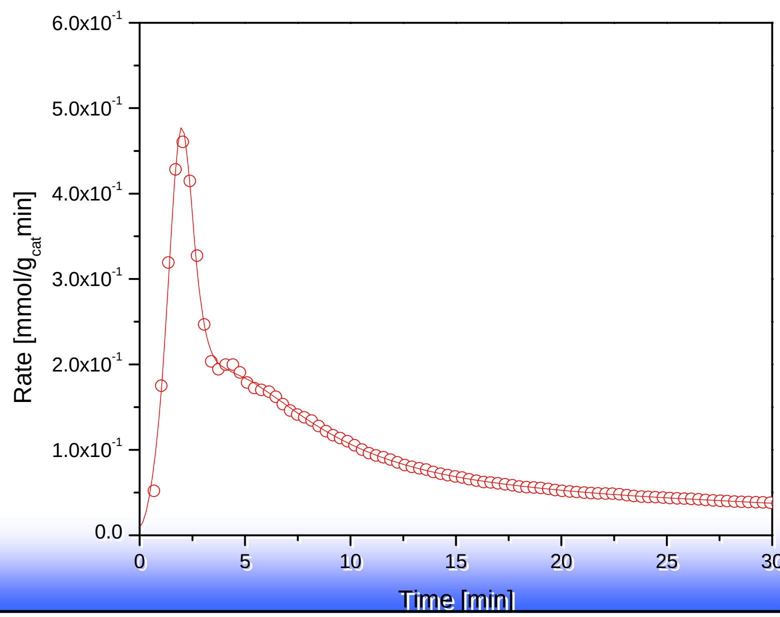
b) Hindrance of Nanotube Displacement



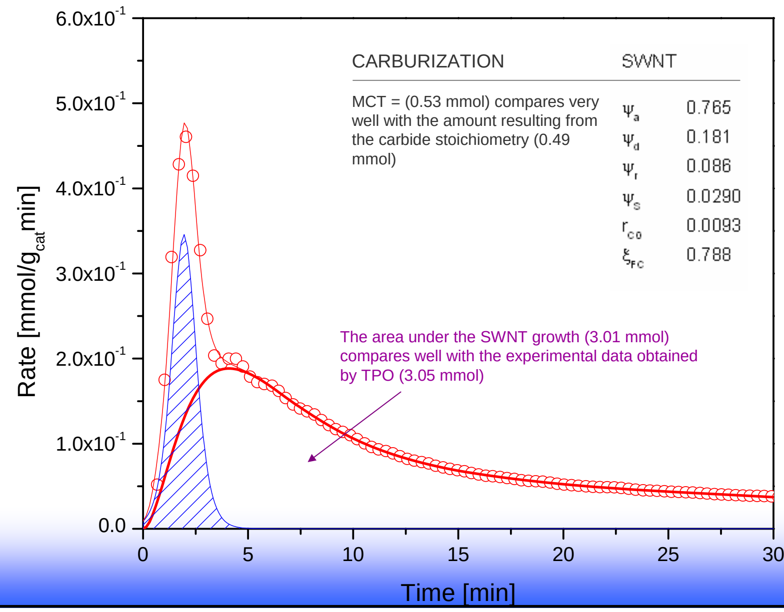




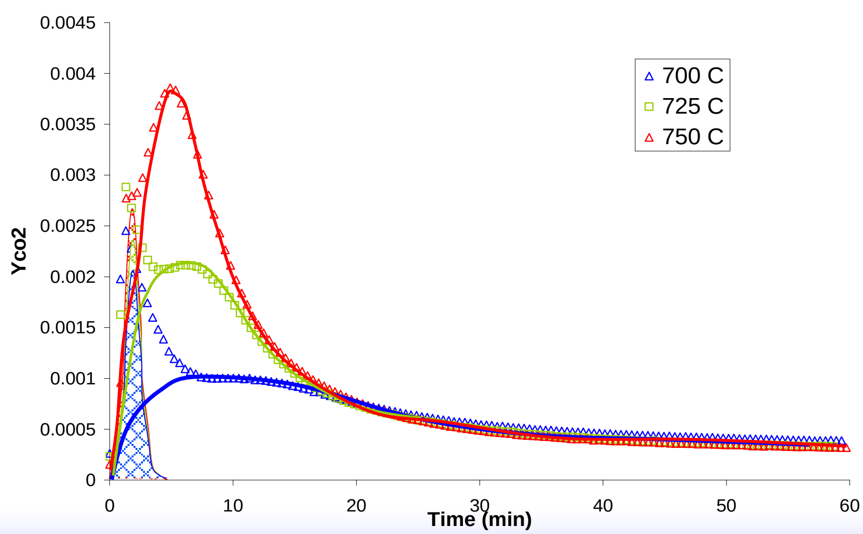
Model Fitting of Experimental Data



Model Fitting of Experimental Data

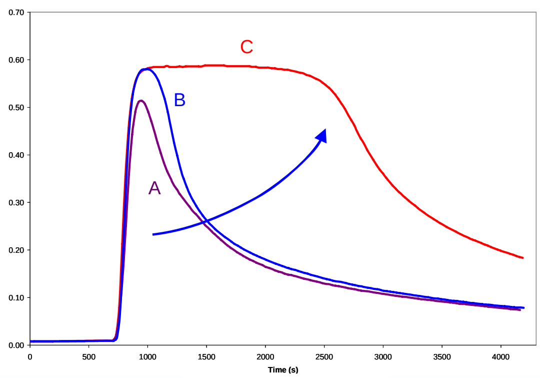


Rate Evolution at Different Temperatures



Rate Evolution as a Method for Catalyst Screening

Control of catalyst and operating conditions allows us to produce different grades of SWNT in a consistent and reproducible manner.



Controlled variations in catalyst and support composition

- Catalyst A
- Catalyst B
- Catalyst C

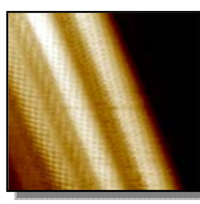
a) Activation rate is similar

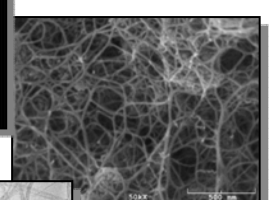
b) Rate of growth termination dramatically varied

Commercial Grades Produced by SWeNT

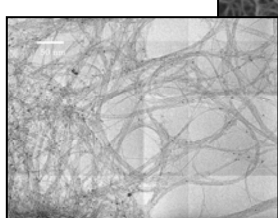
SWeNT

•Standard CoMoCAT Grade (SG):
-**Narrow diameter and chirality distribution (rich in (6,5))**
- d ~ 0.8 nm



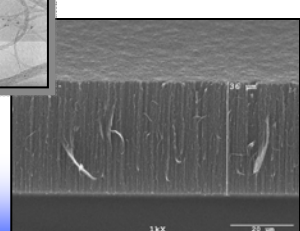


•Specialty Grade for Composites (SGC):
- developed for a strategic partner



•Vertically aligned forests (FG)
small quantities

•Commercial Grade (CG):
- d ~ 0.9-1.1 nm
- **Broader chirality distribution**
- **Low-cost large scale production (2008)**



Quality Control

- Definition of Quality:
  - ISO 9000 - *"Degree to which a set of inherent characteristic fulfills* ***requirements***"
- Working with Strategic Partners:
  - *Specify requirements for each specific customer*
  - *Establish test methods to measure quality parameters*
  - *Meet requirements consistently*
- Continuous Improvement
  - Determine relationship between process variables and quality parameters
  - Implement changes in process that result in optimum quality parameters

Example of Specification for a Customer

- 3.1) Chemical Composition: Chemical composition shall conform to the following percentages by weight, determined in accordance with one of the following methods:
  - by wet chemical methods as described in Appendix A
  - by Thermogravimetric Analysis as described in Appendix B
  - by other analytical methods approved by Customer.
- The composition shall be as follows:
  - Carbon: > XX % - metals combined <XX % Total of Other elements: < XX%
- 3.2) Thermogravimetric response: A sample from each lot shall conform to the following requirements, when tested in accordance with the TGA procedure of Appendix B:
  - Parameter T1: >XX % Residual Mass at 625C: < XX %
- 3.3) Optical absorption: A sample from the lot shall conform to the following requirements, when tested in accordance with the TGA procedure of Appendix C:
  - S2B: > XX
- 3.4) Form: The material shall be in the form of a freeze dried powder, capable of being re-dispersed in aqueous detergent solution using horn sonication. The non-solid content shall be less than 2 wt% as determined by either the method of Appendix A, or by the mass loss in TGA (appendix B) below 210C
- 3.5) Packaging: Material shall be packaged in sealed, re-sealable containers, so as to be protected from shipping damage and contamination, and so as to allow for removal of the material from the container to facilitate use.
- 3.5.1) Labeling: Each material container shall be permanently labeled. The label shall display at least the following information:
- - "Carbon Nanotube Powder"; Supplier name; - Specification number and revision; Lot number; Date of manufacture; Mass of material within container when shipped

Parameter Definitions – Raman quality parameter λ

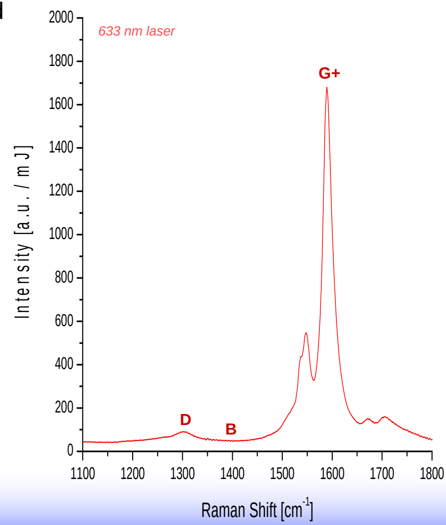
The Raman quality parameter λ is defined as:

$$\lambda = 1-\left(\frac{D - B}{G - B}\right)$$

where:

D is the max height of the D band
G is the max height of the G⁺ band
B is the baseline, taken as the lowest point between the two bands.

λ is a measure of overall quality and particularly to the low levels of amorphous carbon relative to CNT.

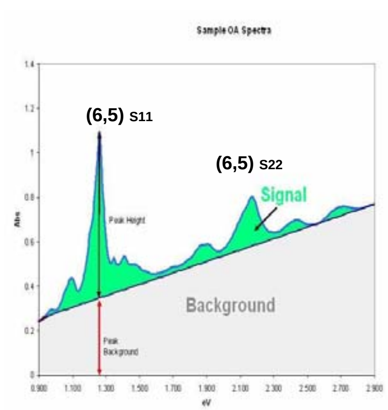


Parameter Definitions – Optical Absorption S2B and P2B

The quality parameters from Optical Absorbance measurements are defined as:

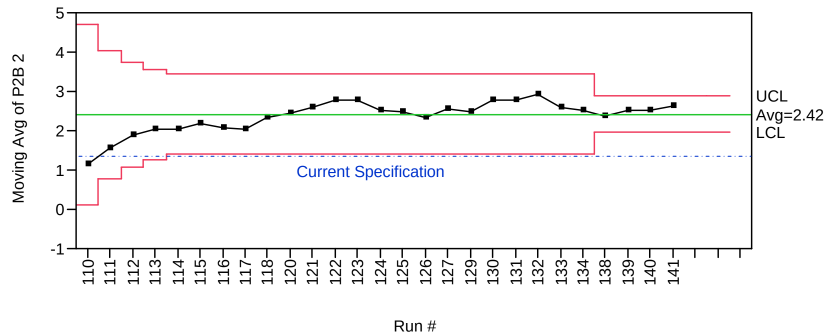
$$S_{2B} = \left(\frac{\textbf{Total Resonance area}}{\textbf{Total Background area}}\right)$$

$$P_{2B} = \left(\frac{\textbf{Height of 6,5 } S_{11} \textbf{ Peak}}{\textbf{Height Peak Background}}\right)$$

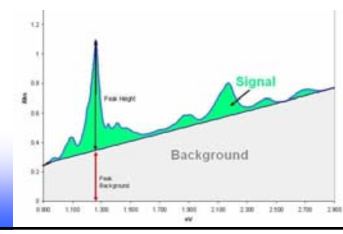


Important: Graph as a function of energy, so background is approximately linear

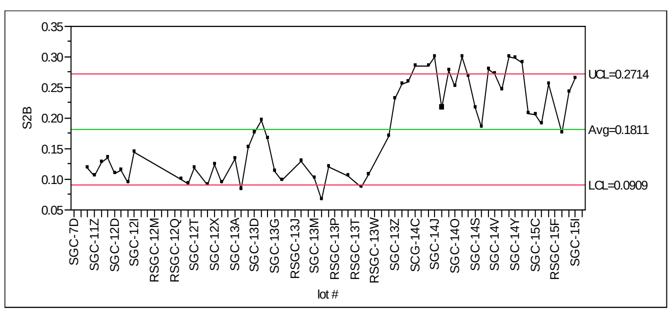
Continuous Improvement Chart for SWeNT® SG



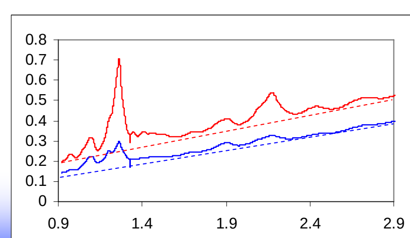
$$P2B = \frac{\textbf{Height of (6,5) } \mathbf{S_{11}} \textbf{ Peak}}{\textbf{Height Peak Background}}$$



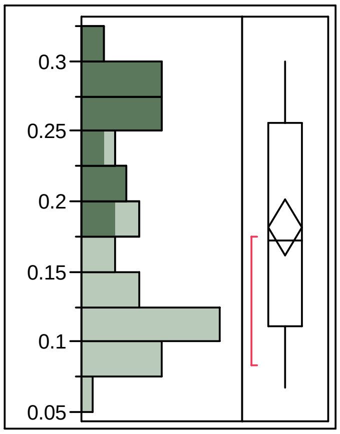
Fixing Operating Conditions for SWeNT® SGC



$$S_{2B} = \left(\frac{\textbf{Total Resonance area}}{\textbf{Total Background area}}\right)$$



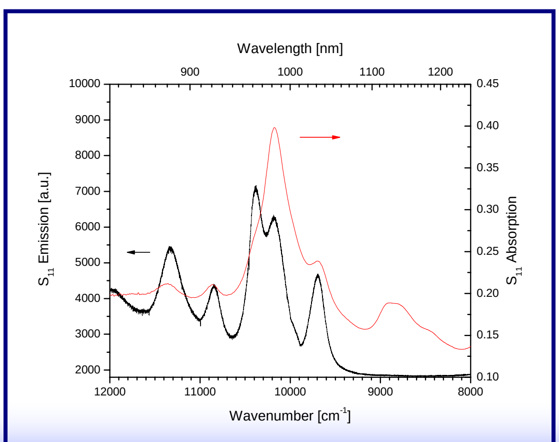
Consistent Data allows for Statistical Analysis



Mean	0.1811232
Std Dev	0.0751126
Std Err Mean	0.0100373
upper 95% Mean	0.2012385
lower 95% Mean	0.1610079
N	56

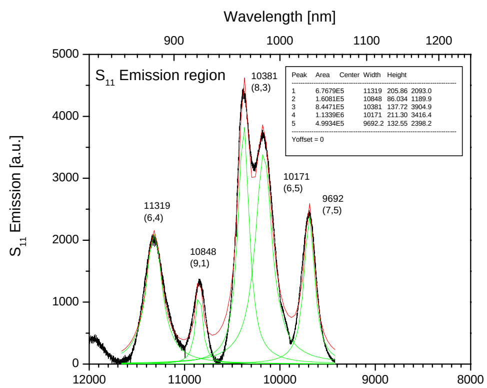
(n,m) species present in SG sample

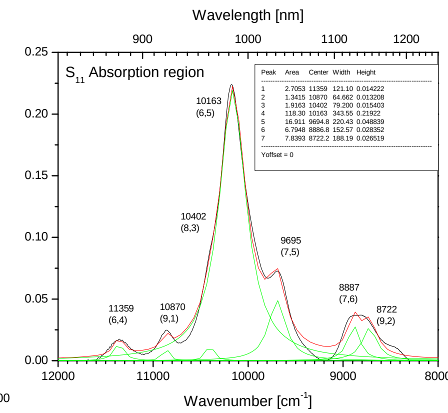
Fluorescence / Optical Absorption



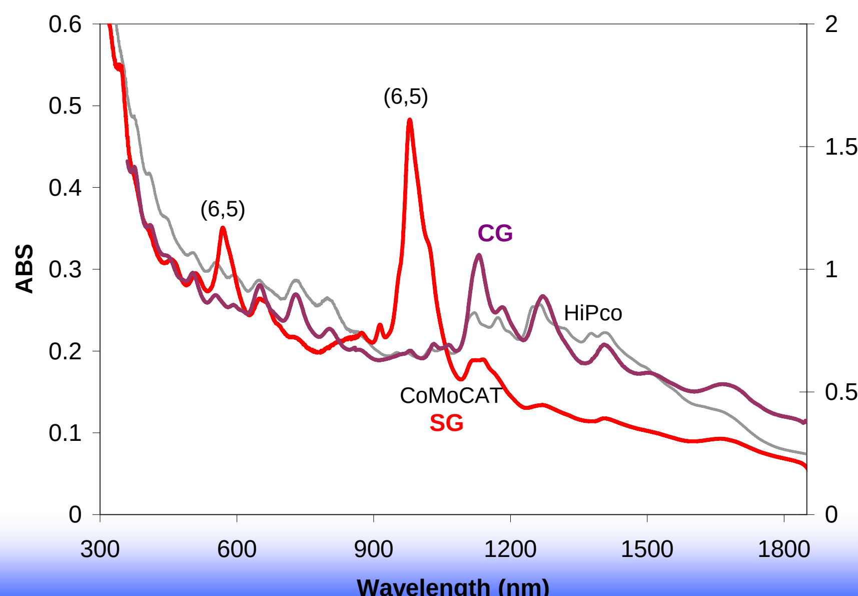
(n,m) species present in SG sample

- Identify nanotubes present in sample with Fluorescence.
- Determine population from S11 Absorption (deconvolution).

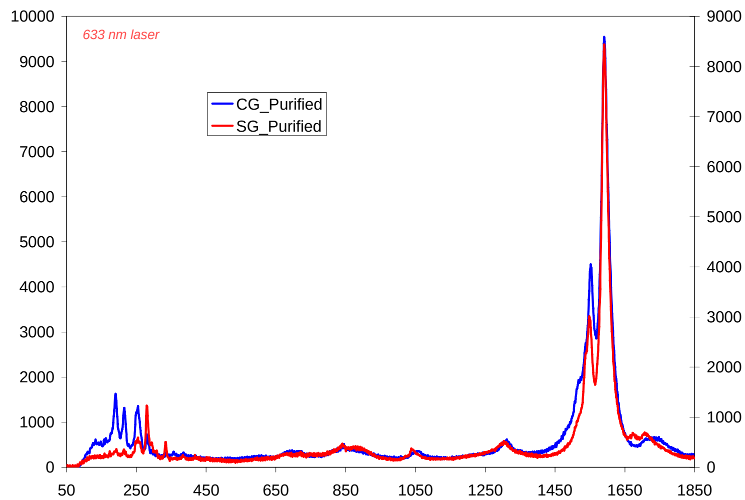




(n,m) species present in SG and CG samples



Raman spectra of SG and CG samples



Parameter Definitions – Thermogravimetry (TGA)

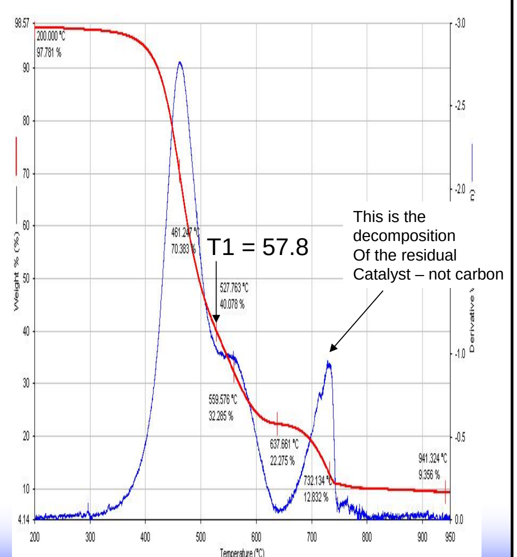
Parameters definitions:

A) % Peak 1:

After fitting TGA derivative profile with Gaussians.

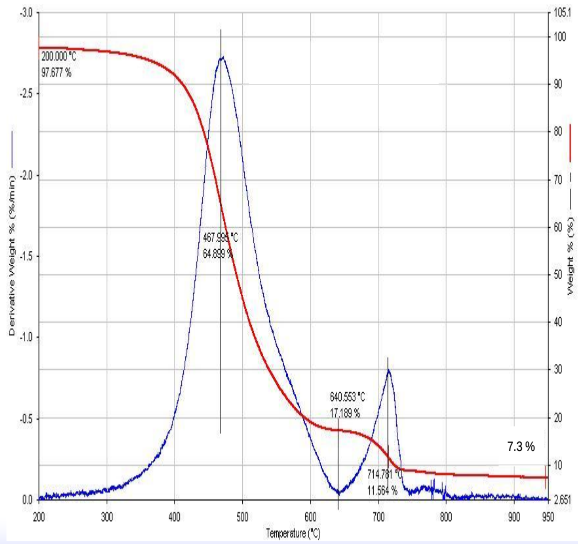
B) T1:
% mass lost at T below first minimum or point of inflection

Note: Position of first peak in derivative depends on type of SWNT and method used to dry sample.



Parameter Definitions – Ash Content by TGA

Ash content is determined as the minimum value of the % weight between 900 and 950°C

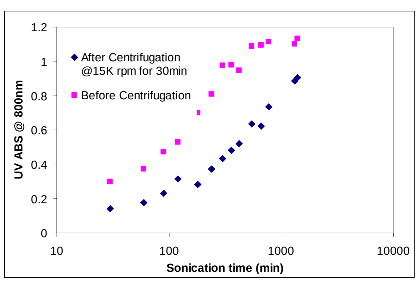


Parameter Definitions – Suspendability

10 mg SWNT / 100 ml

Horn Sonicator: 20 KHz – 20 % amplitude - cooling in ice

Sonication in NaDDBS - SWNT dispersion

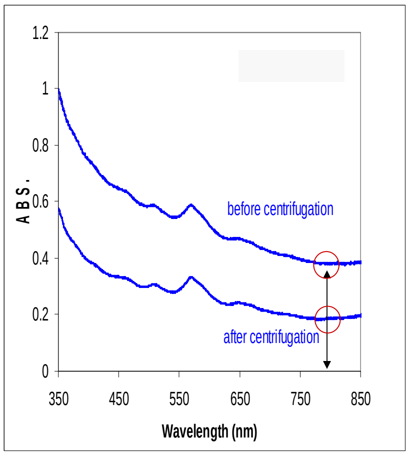


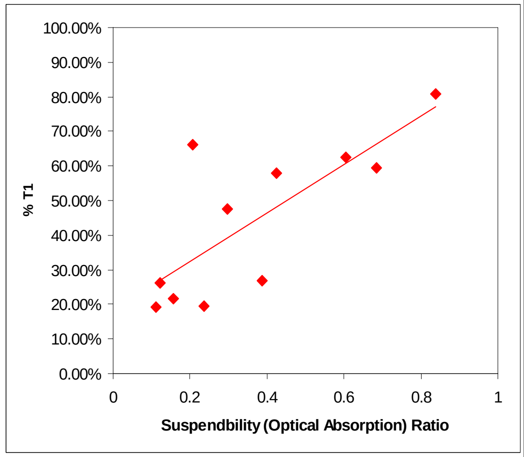
Recommendation:

Always specify:
Sonication method (Horn Vs. Bath)
Sonicator Power and Frequency
Liquid of Volume

- pH of solution
- Cooling method
- SWNT concentration

Parameter Definitions – Suspendability





- This ratio is a good indication of the dispersibility of sample
- There is a good correlation with TGA parameter (T1)

Summary

- Kinetic model captures the main phenomena taking place during SWNT synthesis by the CoMoCAT method
  - Carburization of the pre-reduced oxidic phase
  - Generation of active sites
  - CO dissociation over the surface of the reduced Co cluster
  - Nucleation and growth of SWNT
  - Growth Termination (Catalyst Deactivation, Hindrance Effect)
- By varying catalyst and operating conditions around the same technology, four different commercial products have been developed (SG, SG-C, CG, FG)
- Product quality is being defined, measured, and controlled in terms of requirements (quality parameters) agreed with specific customers.
- Further refining/development of quality parameters (e.g. metallic/semiconducting ratio, nanotube length, etc.) is needed. Research on characterization, purification, (n,m) separation, etc.

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